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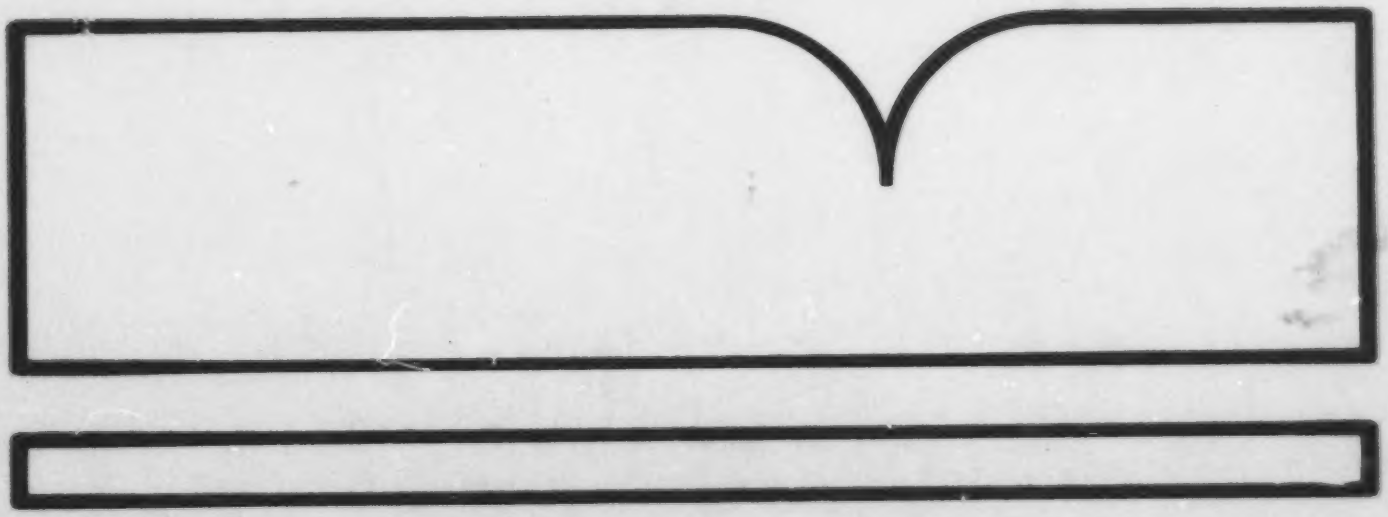

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16. ABSTRACT

Eighteen instruments for measuring atmospheric concentrations of nitric acid were compared in an 8 day field study in the eastern Los Angeles Basin in September 1985. For all sampling periods, reported values for nitric acid varied by a factor of 2 or more. The differences among measurement techniques increased with nitric acid loading, corresponding to a coefficient of variation of 40%. Overall, the highest concentrations are from the filter packs, lower concentrations are given by annular denuders and tunable diode laser absorption spectrometers (TDLAS). In the absence of a continuous reference standard, methods are compared to the average of four denuder difference samplers (DDM). Filter pack samplers are higher than the DDM for both daytime and nighttime sampling. Two different filter packs using Teflon prefilters are higher than the DDM by factors of 1.25 and 1.4. The three annular denuders did not given the same results; the ratio of means to the DDM value are 1.0, 0.8, and 0.6. For the transition-flow reactor method, and for two dichotomous samplers operated as denuder difference samplers, the ratio of means to the DDM are 1.09 and 0.93, respectively. The TDLAS gave low daytime results (TDLAS/DDM = 0.77) and high nighttime results (TDLAS/DDM = 1.65).

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THE NITRIC ACID SHOOTOUT: FIELD COMPARISON OF MEASUREMENT METHODS

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Abstract—Eighteen instruments for measuring atmospheric concentrations of nitric acid were compared in an eight day field study at Pomona College, situated in the eastern portion of the Los Angeles Basin, in September 1985. The study design included collocated and separated duplicate samplers, and the analysis by each laboratory of a set of quality assurance filters, so that the experimental variability could be distinguished from differences due to measurement methods.

For all sampling periods, the values for nitric acid concentrations reported by the different instruments vary by as much as a factor of four. The differences among measurement techniques increase with nitric acid loading, corresponding to a coefficient of variation of 40%. In contrast, samplers of the same design operated by the same group show variability of 11–27%.

Overall, the highest reported concentrations are observed with the filter packs and lower concentrations are observed by the annular denuders and tunable diode laser absorption spectrometers. When the nitric acid concentrations are high enough to be detected by the FTIR, the FTIR values are close to those obtained by the denuder difference method and to the mean value from the other sampler groups.

In the absence of a reference standard for the entire study, measurement methods are compared to the average of four denuder difference method samplers (DDM). Filter pack samplers are higher than the DDM for both daytime and night-time sampling. Two different filter packs using Teflon® prefilters are higher than the DDM by factors of 1.25 and 1.4. The results from the three annular denuders do not agree; the ratios of means to the DDM value are 1.0, 0.8 and 0.6. For the transition flow reactor method and for two dichotomous samplers operated as denuder difference samplers, the ratio of means to the DDM are 1.09 and 0.93, respectively. The tunable diode laser absorption spectrometers gave lower daytime and higher night-time readings compared to the DDM, especially during the last three days of the study. Averaged over the entire measurement period, the daytime ratio of TDLAS to DDM is 0.8 and the night-time ratio is 1.7.

Key word index: Comparison of measurement methods, measurement precision and accuracy, nitric acid.

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OVERVIEW

The Nitrogen Species Methods Comparison Study was a jointly sponsored atmospheric field study conducted in the Los Angeles basin in September 1985. The principal objective was to evaluate, under field conditions, the differences among various techniques used for measuring atmospheric concentrations of nitrogenous species. In this work we present the nitric acid results for 18 different instruments.

Instruments for measuring nitric acid were operated side by side for an eight day period, from 11–19 September 1985, on the Pomona College campus in Claremont, CA. Continuous methods for nitric acid included Fourier transform infrared spectroscopy (FTIR, Tuazon *et al.*, 1981), tunable diode laser absorption spectroscopy (TDLAS, Schiff *et al.*, 1983), and the tungstic acid technique (TAT, Braman *et al.*, 1982). Time integrated techniques included filter packs (FP), the denuder difference method, (DDM, Shaw *et al.*, 1982; Appel *et al.*, 1981), the annular denuder method (ADM, Possanzini *et al.*, 1983), and the transition flow reactor (TFR, Knapp *et al.*, 1986).

Other nitrogen species measured during this study included total and fine particle nitrate, ammonia, particulate ammonium ion, nitrous acid, nitrogen dioxide, peroxyacetyl nitrate and the nitrate radical. Routine air quality and meteorological parameters such as ozone, temperature and relative humidity were monitored. This paper will review results only from the nitric acid data.

Some of these nitric acid methods were also compared in the 1979 Claremont study (Spicer *et al.*, 1982). In that study attention was directed toward artifacts arising from the facile conversion between particulate and gaseous nitrates. In the present study attention is also given to differences between daytime and nighttime measurements, and to short-term vs long-term sampling.

STUDY DESIGN

In addition to the differences among measurement methods, there are two other sources of variability in the field study which required evaluation. First, with so many samplers, it was not possible to use a common sampling manifold. The samplers were sited in a 43 m × 12 m area. Therefore, the influence of sampler siting had to be investigated. Second, the samplers were operated by different groups, each of whom were responsible for their own chemical analyses. Hence variability in chemical analyses needed to be assessed.

The study consisted of four parts:

(1) Interlaboratory comparison of analysis of Teflon® and nylon quality assurance filters containing known amounts of nitrate and sulfate.

(2) Replicate measurements with instruments of the same design and from the same research group, located at different positions on the sampling platform.

(3) Side-by-side sampling with all instruments in the field over an 8-day period.

(4) Simultaneous measurements of meteorological data and of potential interferents such as PAN and nitrous acid.

The analysis of quality assurance filters (No. 1) allows us to assess variability not attributable to the sampling method, while replicate units (No. 2) allow us to assess variability due to instrument siting. The side-by-side sampling (No. 3) includes variability due to measurement method, instrument siting and chemical analysis.

NITRIC ACID MEASUREMENT METHODS

The measurements at the site are summarized in Table 1. Most of the nitric acid measurement methods fall into one of eight categories. Time-integrated samples were collected by (1) filter packs, (2) denuder difference samplers, (3) annular denuders and (4) the transition flow reactor. Continuous and semi-continuous methods include (5) tunable diode laser absorption spectroscopy, (6) Fourier transform infrared spectroscopy, (7) tungstic acid hollow tube denuder collectors, and (8) a luminol method for nitric acid. Descriptions of these methods are given in Appendix A.

The configuration for each sampler is outlined in Table 1. The method used to obtain a fine particle precut is indicated by "Cy", "Imp" or "El" for cyclone, impactor and elutriator, respectively. The types of filters used are given by "T" for Teflon®, "N" for nylon, "Ox" for oxalic acid impregnated, etc. The MgO denuders are shown as "D(MgO)", the carbonate denuders by "D(Na_2CO_3)". The research groups are identified by the principal investigator(s). The first letter in the sampler number is the identifier for the research group; the second letter indicates the measurement method.

SAMPLING SITE AND MEASUREMENT PROTOCOL

Sampling was conducted at the Pomona College campus in Claremont, CA, located in the eastern portion of the Los Angeles Basin. The site was situated in an unused parking lot along the southeastern edge of the campus. Except for the two diode laser systems and one of the tungstic acid tube systems, all of the instruments were located outside. Most were placed in a line along a 1 m high, 43 m long platform oriented perpendicular to the prevailing afternoon winds. Sampling inlets were positioned 1.5 m above the sampling platform (2.5 m above the ground). The FTIR operated with a 25 m open path located 3 m in front of the platform and 2.5 m above the ground. Thus all sampler inlets and the FTIR basepath were 2.5 m above the ground. This configuration was used to minimize the influence of possible vertical concentration gradients.

Table 1. Sampler descriptions (Nitrogen Species Methods Comparison Study, September 1985, Pomona College, Claremont, CA)

Group	ID	Sampler	Inlet	Holder	(ℓ min^{-1})	Species
Filter packs						
Anlauf/Wiebe	CF1	-T/N/Citric acid	—	T	40	HNO_3, NO_3^-, NH_3, NH_4^+, SO_4^{2-}
	CF2	-T/N/Citric acid	—	T	40	HNO_3, NO_3^-, NH_3, NH_4^+, SO_4^{2-}
Eatough	EF1	-Imp-Q/N	P&G	T	10	HNO_3, NO_3^-, NH_4^+, HNO_3
Cass/Solomon	GF1	-T/N, -T/Ox/Ox	—	P	3, 4.5	HNO_3, NO_3^-, NH_3, NH_4^+, SO_4^{2-}
	GF2	-T/N, -T/Ox/Ox	—	P	3, 4.5	HNO_3, NO_3^-, NH_3, NH_4^+, SO_4^{2-}
	GF3	-T/N, -T/Ox/Ox	—	P	3, 4.5	HNO_3, NO_3^-, NH_3, NH_4^+, SO_4^{2-}
	GF4	-T/N, -T/Ox/Ox: (network)	—	P	3, 4.5	HNO_3, NO_3^-, NH_3, NH_4^+, SO_4^{2-}
Grosjean	MF1	-N/N & -T/N	—	P	20	Total nitrate, oxalate
Marlin/Mitchell	JF1	-T/N/K_2CO_3	—	T	4	HNO_3, NO_3^-, SO_2, SO_4^{2-}
	JF2	-T/N/K_2CO_3	—	T	4	HNO_3, NO_3^-, SO_2, SO_4^{2-}
Womack	NF1	El-T/N/S	T	T	3	HNO_3, NO_3^-, SO_4^{2-}
	NF2	El-T/N/S (6 days/sample)	T	T	3	HNO_3, NO_3^-, SO_4^{2-}
	NF3	El-T/N/S (6 days/sample)	T	T	3	HNO_3, NO_3^-, SO_4^{2-}
	NF4	-T/N/S (6 days/sample)	T	T	3	HNO_3, NO_3^-, SO_4^{2-}
Denuder difference methods						
Appel	AD1	Cy-D(MgO)/N, -Cy-N	T&G	P	20	HNO_3, NO_3^-, SO_4^{2-}
Cass/Solomon	GD1	Cy-{-D(MgO)/N, -N, -T}	G&T	T	3+3+4.5	HNO_3, NO_3^-, SO_4^{2-}
	GD2	Cy-{-D(MgO)/N, -N, -T}	G&T	T	3+3+4.5	HNO_3, NO_3^-, SO_4^{2-}
	GD3	Cy-{-D(MgO)/N, -N, -T}	G&T	T	3+3+4.5	HNO_3, NO_3^-, SO_4^{2-}
Horrocks	FD1	Cy-D(MgO)/T/N, Cy-T/N	T&G	P	20	HNO_3, NO_3^-, SO_4^{2-}
John	BD1	Dichot{T/N, T/N}	Al	Al	16.7	HNO_3, Coarse and fine NO_3^-, SO_4^{2-}, NH_4^+, H^+, Na^+, Ca^{2+}, Cl^-
	BD2	Cy-T/N	G&T	P	24	
	BD3	D(Anodized Al)/Dichot{T/N, T/N}	Al	Al	16.7	
Pierson	KD1	Cy-{-D(MgO)/N, -N} -N	T	SS	10+18, 18	HNO_3, Coarse and fine NO_3^-, SO_4^{2-}
	KD2	Cy-{-D(MgO)/N, -N} -N (1/day)	T	SS	10+18, 18	HNO_3, Coarse and fine NO_3^-, SO_4^{2-}
Annular denuders						
Sickles/Allegrini	IA1	Cy-D{Na_2CO_3, Na_2CO_3, Citric acid)/T/N/D(Citric acid or K1&$NaAsO_2$)	T	T	15	HNO_3, HNO_2, NO_2, NO_3^-, SO_2, SO_4^{2-}
	IA2		—	—	—	HNO_3, HNO_2, NO_2, NO_3^-, SO_2, SO_4^{2-}
Eatough	EA1	Cy-D(Na_2CO_3, Na_2CO_3)/Q/N	T	T	20	HNO_3, HNO_2, NO_2, NO_3^-, SO_2, SO_4^{2-}, $AlkSO_4$
	EA2	Cy-D(Na_2CO_3, Na_2CO_3)/Q/N	T	T	20	HNO_3, HNO_2, NO_2, NO_3^-, SO_2, SO_4^{2-}, $AlkSO_4$
Peake	QA1	Cy-D(Na_2CO_3, Na_2CO_3, Citric acid)/T/N	T	T	14	HNO_3, HNO_2, NO_2, NO_3^-, NH_3, SO_2, SO_4^{2-}
Transition flow reactors						
Ellestad	HE1	Cy-{-D(N,Nafion)/T/N/Ox/TEA/TEA	T	T	18	HNO_3, NO_2, NO_3^-, NH_3, NH_4^+, SO_2, SO_4^{2-}
	HE2	-D(N, Nafion)/T/N/Ox/TEA/TEA}	—	T	18	HNO_3, NO_2, NO_3^-, NH_3, NH_4^+, SO_2, SO_4^{2-}
Spicer	DE1	Cy-{-D(N,Nafion)(T/N/Ox/TEA/TEA	T	T	18	HNO_3, NO_2, NO_3^-, NH_3, NH_4^+, SO_2, SO_4^{2-}
	DE2	-D(N, Nafion)/T/N/Ox/TEA/TEA}	—	T	18	HNO_3, NO_2, NO_3^-, NH_3, NH_4^+, SO_2, SO_4^{2-}
Continuous methods						
Stedman	SC1	Luminol HNO_3	T	T	2	HNO_3
Winer/Tuazon	RC1	FTIR (HNO_3, NH_3)	—	—	—	HNO_3, NH_3

Table 1. (*Contd.*)

Group	ID	Sampler	Inlet	Holder	(ℓ min^{-1})	Species
Anlauf/Wiebe	CC1	T/TDLAS /HNO_3, NO_2)	9'T	T	5	HNO_3, NO_2
Mackay	PC1	T/TDLAS (HNO_3, HCHO)	9'T	T	5	HNO_3, HCHO
Appel	AC1	Tungstic acid tubes	3'G	—		HNO_3, NH_3
Braman	TC1	Tungstic acid tubes	3'G	—	0.7	HNO_3, HNO_2, NO_3^-
Other gaseous species						
Appel	AO1	-D(Ox)	—	—	1	NH_3
Appel	AF1	-T/Ox/Ox	P	P	25	NH_3, NH_4^+
Winer/Biermann	RC2	DOAS	—	—	—	HNO_2, NO_2, NO_3^-
Spicer/Holdren	DC1	PAN-GC		—		PAN
Grosjean	MF2	-KOH/KOH & -DNPH/DNPH	—	P	20	Acids, phenols, PBzN, carbonyls
Grosjean	MF3	-T/KOH & -T/DNPH	—	P	20	Acids, phenols, PBzN, carbonyls
Mackay	PC2	Luminox analyzer	T	—	—	NO_2
Anlauf/Wiebe	CC2	T/N/NO_x box	T	—	—	NO, NO_x(NO + NO_2 + PAN)
Appel	—	Dasibi 1003	—	—	—	O_3
Ellis	—	Gases {O_3, SO_2, NO_x, CO}	—	—	—	O_3, NO_x, CO
Eatough	—	GC-FPD (Dimethylsulfate)	T	—	0.5	$(CH_3O)_2SO_2$
Other aerosol measurements						
John	BO1	Berner low pressure impactor	A1	A1	30	NO_3^-, NH_4^+, SO_4^{2-}, H^+, Na^+, Cl^-, Ca^{2+}, Mg^{2+}
Ellis	OO1	Dichotomous sampler	A1	A1	17	NO_3^-, SO_4^{2-}
Lawson	FO1	HiVol/G	A1	A1	1120	NO_3^-, SO_4^{2-}, TSP
	FO2	HiVol/Q	A1	A1	1120	NO_3^-, SO_4^{2-}, TSP
	FO3	PM10-HiVol/Q	A1	A1	1120	NO_3^-, SO_4^{2-}, PM_{10}
Meteorological measurements						
Appel	—	Temperature, relative humidity	—	—	—	Temp, r.h.
Ellis	—	Temperature, relative humidity, winds, barometric pressure, solar intensity.	—	—	—	Met data
Special experiments						
Eatough	EO3	Im-D(Ox, Ox, Ox, Ox)/Q/N/Ox	P&G	T	2	NO_3^-, NH_3, NH_4^+
	EO2	Im-{-D(TA,TA,TA,TA)/Q/N/Ox	P&G	T	2	HNO_3, NO_3^-, NH_3, NH_4^+
	EO1	Im-{D(N,N,N,N,N,N)/Q/N	P&G	T	2	HNO_3, NO_3^-, $AlkSO_4$, HNO_2
	EO5	-D(N)/Q/N}	P&G	T	10	HNO_3, NO_3^-
	EO7	-D(6 × Na_2CO_3)/Q/N	P&G	T	2	HNO_3, HNO_2, NO_3^-
Ellestad	HO1	Cy-D(N)/T/D(N)/N (4 days/dy-nt pair)	T	T	1.5	HNO_3
Filter tests	TO	-T/N(old Membrana)	—	P	15	HNO_3, NO_3^-, SO_4^{2-}
	TL	-T/N(new, low pressure, drop, no. 871)	—	P	15	HNO_3, NO_3^-, SO_4^{2-}
	TH	-T/N (new, high pressure, drop, no. 4195)	—	P	15	HNO_3, NO_3^-, SO_4^{2-}
Deposition measurements						
John	BO2	Plants & artificial surfaces	—	—	—	NO_3^-, SO_4^{2-}
Pierson	KO1	Dew collectors	—	—	—	HNO_3, NO_3^-, SO_4^{2-}
Pierson	KO2	Surrogate surfaces	—	—	—	HNO_3, NO_3^-, SO_4^{2-}

Table 1. (*Contd.*)

Group	ID	Sampler	Inlet	Holder	(ℓ min^{-1})	Species
Atmospheric mutagens						
Winer/Atkinson	RX1	MegaVol/TIGF & G	Al	Al	17900	Mutagenicity & nitroarenes
	RX2	PM 10-HiVol/TIGF	Al	Al	1120	Mutagenicity & nitroarenes
		PM10-HiVol/G	Al	Al	1120	Mutagenicity & nitroarenes
	RX3	Tenax columns	—	—	2	Reactivity of pyrene & fluoranthene

T, Teflon®; G, glass; Al, aluminum; P, plastic; Q, quartz filter; N, nylon filter; Ox, oxalic acid impregnated filter; TA, tungstic acid; TEA, triethanolamine impregnated filter; TIGF, Teflon® impregnated glass fiber filter; AlkSO_4, alkylated sulfates; PBzN, peroxybenzoylnitrate.

During the first two days of the study, all replicate instruments, i.e. identical instruments operated by the same group, were positioned side by side. For the remaining six days of the study, several of the replicate instruments were sited at different positions along the platform. This design permitted evaluation of differences due to sampling location.

The sampling schedule was designed to accommodate the needs of both short-term and long-term samplers. It was felt that each sampler should be tested in the mode for which it was designed. Thus investigators were given the choice of one of three schedules, consisting of five, two or one sampling period per day. Each investigator was asked to follow the same sampling schedule throughout the study. The five-per-day schedule consisted of four consecutive 4-h periods starting at 0800 PDT, followed by one 6-h period from midnight to 0600. These periods were selected to coincide with peak concentrations of various species during each day. The two-per-day schedule had one 12-h sampling period from 0800 to 2000 and one 10-h period from 2000 to 0600 the following morning. The one-per-day schedule ran from 0800 to 0600 the following morning. Samples were not collected between 0600 and 0800. This time was used for instrument calibration checks and the collection of field blanks. Some groups ran with identical samplers on different schedules to assess the effect of sampling duration.

QUALITY CONTROL CHECKS: QUALITY ASSURANCE FILTERS AND REPLICATE SAMPLERS

Quality assurance filters

Thirteen of the groups in the study relied on ion chromatographic analyses for integrated measurements of nitric acid and particulate nitrate. Since each laboratory analyzed its own filters, the consistency among laboratories was checked by asking each group to analyze a set of quality assurance filters upon which known amounts of sulfate and nitrate had been deposited. The quality assurance filters were prepared by Columbia Scientific Industries (Austin, TX). Each set consisted of nine Teflon® filters (1 μm pore Zefluor, Gelman Sciences, Ann Arbor, MI) and nine nylon filters (1 μm Nylasorb, Gelman Sciences). Nitrate loadings on the Nylasorb filters, as specified by Columbia Scientific Industries, were 9.90 ± 0.01 μg, 69.0 ± 0.15 μg and 197.7 ± 0.5 μg. The nitrate loadings on the Zefluor filters were 24.85 ± 0.04 μg, 74.85 ± 0.14 μg, and 249.3 ± 0.6 μg. Laboratories were provided with three filters at each level of ion loading.

The results for nitrate analysis of the nylon quality assurance filters are shown in Table 2. Data for each nitrate loading are listed by the filter series number (100, 200 and 300). The average value from the analytical laboratories is generally in good agreement ($\leq 4\%$ deviation) with the deposited nitrate loadings, with the exception of the lightly loaded, series 100

Table 2. Comparison of nitrate analysis on nylon quality assurance filters

	Accuracy % Deviation from deposited value			Measurement precision Coefficient of variation (%)			
Laboratory*	Ser. 100	Ser. 200	Ser. 300	Ser. 100	Ser. 200	Ser. 300	Pooled
A	−29	−02	−02	9.4	0.9	0.6	0.5
B	14	01	−06	2.9	3.1	3.6	2.6
C	01	−02	00	1.5	0.5	0.3	0.3
D	34	16	06	2.3	1.6	4.8	3.4
E	21	00	−07	0.8	0.4	0.3	0.3
F	01	05	−11	3.6	5.8	0.9	1.7
G	−08	02	04	3.4	0.5	0.6	0.4
H	05	02	01	1.1	0.3	0.3	0.2
I	−63	−29	−18	5.7	1.7	1.3	1.1
J	−92	−02	−02	173.	2.4	5.5	4.2
K	−02	01	−03	1.2	0.7	1.7	1.2
M	08	02	01	1.9	0.5	0.0	0.1
N	−57	−32	−16	0.0	3.7	3.5	2.8
Q	−03	01	00	2.6	1.1	0.3	0.4
Deposited value ($\mu g\ NO_3$)	9.9	69	198	9.9	69	198	
% Deviation of average from deposited value	−12	−03	−04				

* Designation letters are the same as the first letter of the sampler ID listed in Table 1.

Nylasorb filters. Except for groups B and C (who used large sampling volumes), the series 100 filters are representative of the amount of nitrate collected during many of the night-time sampling periods. The accuracy of the analytical laboratories is presented in terms of the percentage deviation from the deposited value. For the filters loaded with 69 and 198 μg (series 200 and 300), 17 of 28 values agree within 3% of the deposited loading; all but one group report values within 11%. For filters loaded with 9.9 μg of nitrate (series 100), only seven of the 14 groups report values within 8% of the deposited loading. The values from two laboratories are low at all three nitrate loadings. These two groups, N and I, used deionized water for the filter extractions, whereas all other laboratories used eluent or basic solution. For groups N and I, the sulfate levels for the lightly loaded Nylasorb are also low; however, their results for both nitrate and sulfate on the Zefluor (Teflon®) filters are within 2% of the deposited value in one case, and within 15% in the other.

The precision of the individual laboratories is given by the coefficient of variation for analyses of three filters at each level of deposited nitrate. Generally the precision of the laboratories is good. For the series 200 and 300 filters, coefficients of variation are less than 6% for all fourteen laboratories, and nine of the laboratories have coefficients of variation less than 1%. For the series 100 filters (with 9.9 μg of deposited nitrate), twelve laboratories report standard deviations of less than 0.4 $\mu g\ NO_3^-$ filter. Analytical precision, calculated using twice the pooled standard deviation divided by the appropriate sample volumes for each group, is better than 25 neq m^{-3} for all groups except D, J and N.

Some of the nylon filters used by participants were older filters manufactured by Membrana (Pleasanton, CA). Others were newer filters purchased from Gelman, following the sale of the Membrana company to Gelman. The newer Gelman filters were somewhat different in appearance, and often had a larger pressure drop for the same face velocity. The old Membrana filters and two lots of the new Gelman filters were compared in side-by-side sampling with filter packs (sampler nos TO, TL, and TH in Table 1). No differences were observed in the collection efficiency for HNO_3, although the new filters did retain some SO_2.

Replicate samplers

Before assessing the differences among samplers, we must first ask how precise the measurement is for a specific sampler type. There were five pairs of replicate samplers in the study. Two of these like sampler pairs, namely the CIT filter packs no. GF1 and no. GF3 and the Canadian filter packs no. CF1 and no. CF2, were located side-by-side for the first two days of the study, and then were sited at different locations on the platform for the remainder of the study. The other three like sampler pairs were collocated throughout the study. The collocated measurements are indicative of the overall precision, including both sampling and analysis, which can be expected from the method, whereas the separated measurements include the increased variability due to sampler siting.

For collocated sampling, the standard deviations within sampler pairs are, respectively, 15, 49, 15, and 25 neq m^{-3} for filter packs no. GF1 and no. GF3, denuder difference samplers no. GD1 and no. GD3, annular denuders no. IA1 and no. IA2, and TDLAS systems no. CC1 and no. PC1. The corresponding coefficients of variation are 12, 27, 35 and 20%.

Data from the separated CIT filter packs no. GF1 and no. GF3 are shown by the solid symbols in Fig. 1.

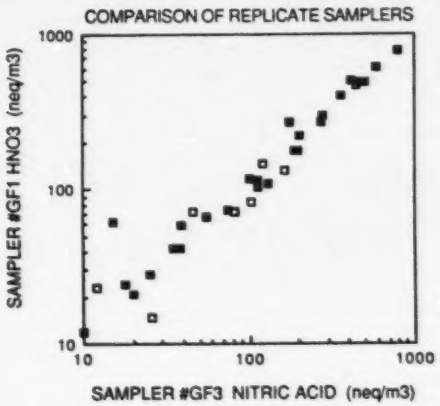

Fig. 1. Comparison of simultaneous 4- and 6-h nitric acid data obtained from two filter packs of the same design, operated by the California Institute of Technology. Data are shown for collocated (□) and separated (■) siting of the samplers along the instrument platform.

A linear least squares regression gives a slope of 1.03 and a correlation coefficient of 0.99, indicating no systematic bias due to sampler location on the platform. The coefficient of variation between the two samplers is 12%, which is the same value observed when the filter packs were collocated, and approximates the precision expected on the basis of the CIT quality assurance filter data and sample volumes. Similarly, the coefficient of variation between the separated Canadian filter packs was 15%. Therefore, the siting of the samplers on the platform did not introduce a systematic bias, nor did it contribute significantly to the scatter in the data.

STUDY RESULTS: DATA PRESENTATION

Time series plots of the nitric acid concentrations measured during the study are shown in Figs 2 and 3. These are grouped according to measurement method, with filter pack data and denuder difference method results in Fig. 2, and the annular denuders, the transition flow reactors, diode lasers and the tungstic acid hollow tube methods in Fig. 3. (FTIR data are available for a only small part of the study, and are presented in a later section.) The data all show the same trends, with clear diurnal variations in the nitric acid levels and peak daytime nitric acid concentrations on 14 September 1985.

Several results are apparent from inspection of the data. For the most part, the variation among sampling periods is greater than the differences among measurement methods. The highest reported nitric acid concentrations are from the filter packs. For example, on the high nitric acid day of 14 September, values reported by most filter packs are higher than those observed by the diode laser systems. Results from the denuder difference methods on this day are intermediate.

Comparing samplers within each sampler type, we find that the 4- and 6-h filter pack samplers agree reasonably well. The same is true of the denuder difference samplers, the two transition flow reactors and the two laser diode spectrometers. There is somewhat more scatter among the three annular denuders. Large discrepancies are observed between the two tungstic acid technique systems. These were not identical systems. The two TAT samplers were constructed and operated by different groups. While using the same principle for nitric acid detection, the systems differed in their inlet design and in the operational procedure.

The standard deviation in the reported nitric acid concentration for each sampling period among all of the instruments shown in Figs 2 and 3 is plotted in Fig. 4. For both the 10- and 12-h sampling and the 4- and 6-h sampling the standard deviation increases linearly with the nitric acid concentration. In both cases the data can be described well by a coefficient of variation of 40%. The corresponding range in reported nitric acid concentrations in a given sampling period is about a factor of four. For example, on the afternoon of 14 September (period 43) reported nitric acid concentrations varied from 190 neq m^{-3} to 800 neq m^{-3}, with all but two samplers giving values between 330 and 800 neq m^{-3}. The differences among samplers are larger than can be explained by the analytical accuracy as indicated by the quality assurance filter analysis, or by the overall sampling precision as indicated by the replicate samplers.

OVERVIEW OF DATA ANALYSIS

Questions addressed in this data analysis are: (1) the systematic differences among individual samplers and among sampling methods, (2) the measurement precision for each sampler and (3) diurnal variations in sampler performance. Two sets of analyses are presented. First the samplers are compared individually, and second, the different measurement methods (e.g. FP vs DDM) are compared. Although the differences between types of methods may be of greatest interest, it is necessary to compare the samplers individually to avoid prejudging the data. The individual sampler comparisons also provided a basis for selecting representative samplers for the intermethod comparisons. Thus the comparison between measurement methods presented here is based on a subset of the data which excludes samplers with imprecise data.

COMPARISONS AMONG INDIVIDUAL SAMPLERS: 10- AND 12-h DATA

To compare the different samplers we have selected a subset of the data for which we have a complete data set. Thus four of the samplers are excluded from this

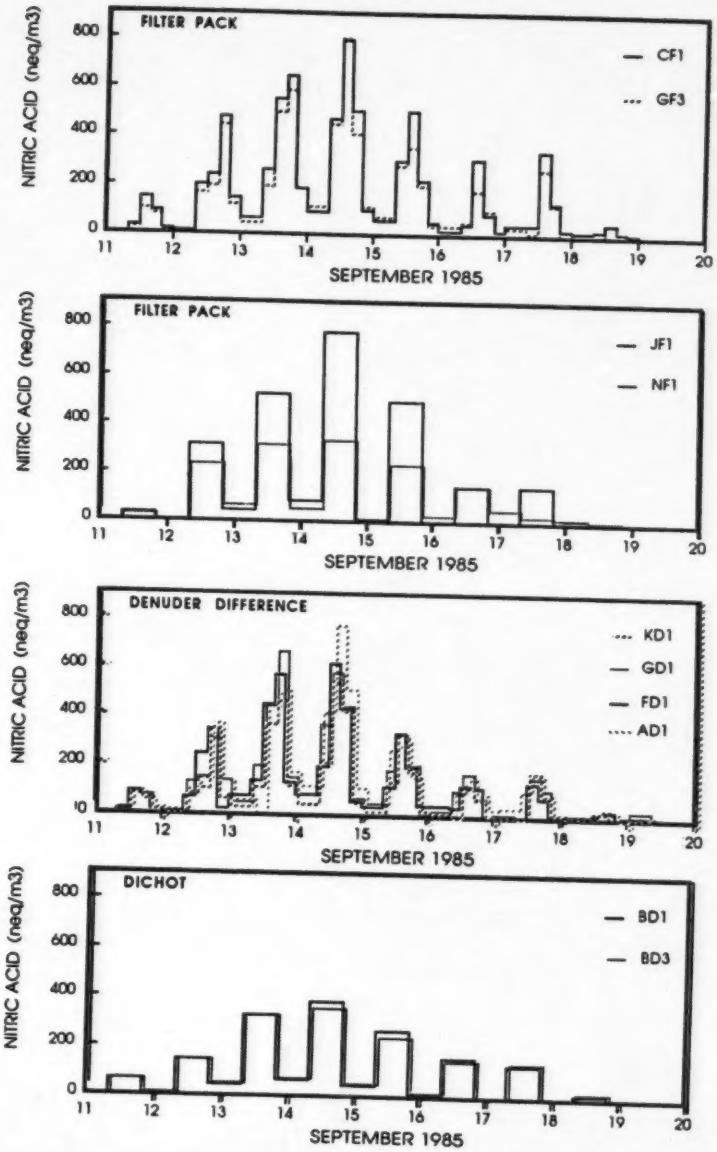

Fig. 2. Time series plots of nitric acid data from filter packs and denuder difference samplers for 10- and 12-h sampling, and for 4- and 6-h sampling. Sampler configurations and identification numbers are given in Table 1.

analysis: the Luminol semicontinuous nitric acid monitor, one TFR (no. DE1), one TAT system (no. AC1), and the FTIR. Replicate samplers of the same design operated by the same group were not included. The data from those samplers collecting 4- and 6-h samples have been composited to provide 10- and 12-h averages for comparison with the half day collection periods.

A total of eighteen samplers are compared over nine half-day sampling periods (nos 16, 26, 27, 37, 46, 47, 56, 57 and 76, as given in Table A2) for which a complete data set was available, and for which median concentrations were above 20 neq m^{-3}. Samplers with 10- and 12-h sampling times include two filter packs (no. JF1 and no. NF1), two dichotomous denuder difference samplers (no. BD1 and no. BD3), and one transition flow reactor (no. HE1). Samplers operating on the 4- and 6-h sampling times, whose data are composited for this comparison, include two filter packs, no. CF1 and no. GF3, four denuder difference samplers, no. AD1, no. FD1, no. GD1 and no. KD1, and two annular denuders, no. IA1 and no. QA1. Continuous data were obtained from the two tunable

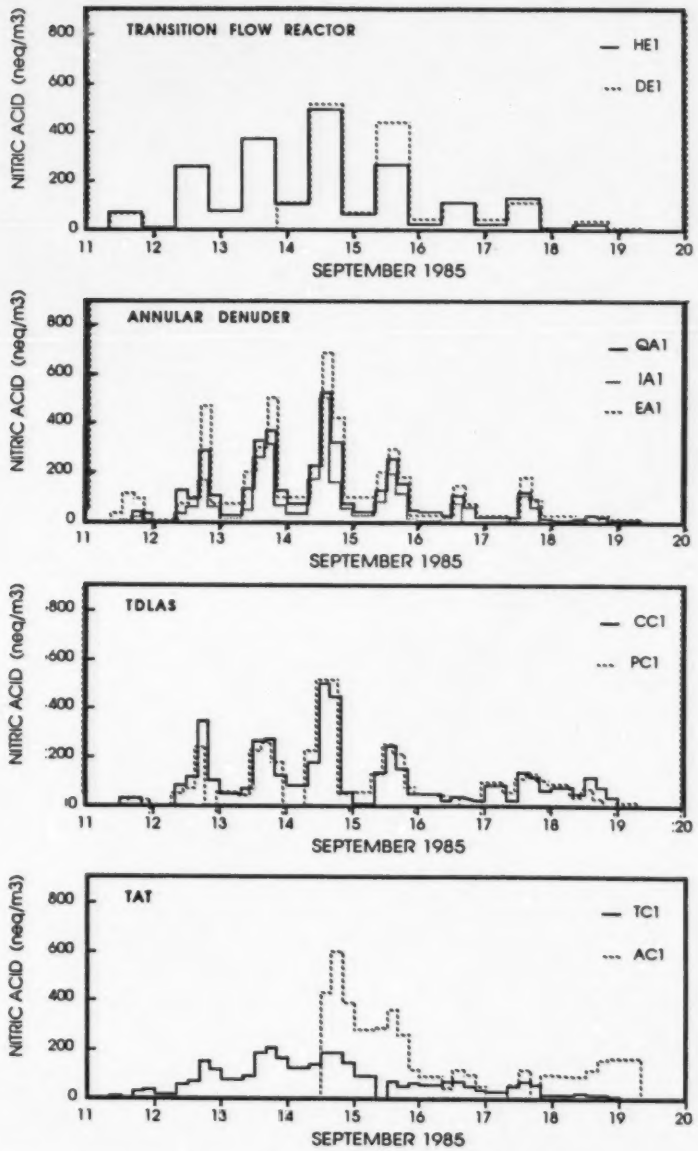

Fig. 3. Time series plots for nitric acid data from transition flow reactors, annular denuders, tunable diode laser spectrometers, and tungstic acid technique systems. Sampler identification numbers are given in Table 1.

diode laser absorption spectrometers, no. CC1 and no. PC1, and from the tungstic acid hollow tube system no. TC1. One filter pack, no. EF1, and one annular denuder, no. EA1, operated on the 4-h schedule during the day, and the 10-h schedule at night. The periods considered include five daytime samples and four night-time samples. The mean nitric acid concentrations ranged from 30 to 440 neq m^{-3}, mean temperatures varied from 17 to 28°C and mean relative humidities were 30–90%.

In this analysis the samplers are considered individually without grouping them by the measurement method. Systematic differences among the samplers are evaluated using the Friedman analysis of variance by rank, which is a distribution-free, non-parametric statistical test (Hollander and Wolfe, 1973). Nitric acid concentrations from each sampler are ranked from highest to lowest for each period, and then the samplers are compared on the basis of their average ranking. One advantage of this particular statistical

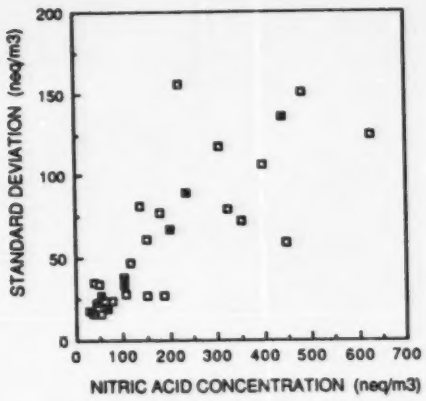

Fig. 4. The standard deviation in the reported nitric acid for all samplers is shown as a function of the average nitric acid concentration for each of the sampling periods. Four- and six-hour sampling is shown by the open symbols (□), 10- and 12-h sampling is shown by the solid symbols (■).

test is that it does not assume that the data are normally distributed. Each sampling period is given equal weight in the analysis.

The Friedman analysis of variance shows there are significant differences among the samplers at a > 99.9% confidence level. The average ranking of the samplers, based on the reported nitric acid concentrations, is shown in Fig. 5. The highest concentrations are from the filter packs no. CF1 and no. GF3. The lowest concentrations are from one of the annular denuders, no. IA1. Pairwise comparisons, based on the Friedman rank sums, show that, at the 95% confidence level, the nitric acid concentrations reported by no. IA1 are lower than those reported by the no. CF1 and no. GF3 filter packs and the no. HE1 transition flow reactor:

no. IA1 < no. CF1
no. IA1 < no. GF1
no. IA1 < no. HE1.

No statistically significant difference is seen among the other samplers with the Friedman analysis.

To assess measurement precision, we worked with the log transformation of the data. The data are much better approximated by a lognormal distribution than by a normal distribution. However, the lognormal distribution is a poor assumption for the low concentration data. When the nitric acid concentrations are less than 25 neq m^{-3} ($\approx$ 0.6 ppb), analytical errors are significant, and therefore these periods are not included in the analysis.

The precision of each of the measurement techniques is assessed by calculating the mean squared residual for each sampler j:

$$R_j = (1/n)\Sigma_i(\mathrm{Log}(S_{ij}/M_i))^2, \quad (1)$$

where S_{ij} is the nitric acid concentration reported by sampler j for period i, and M_i is the geometric mean concentration reported by all 18 samplers for period i, and n is the number of periods. The mean squared residual is the average of the squares of the difference between the logarithm of the sampler nitric acid concentration and the logarithm of the geometric mean concentration among all samplers for the sampling period. It reflects both the random and systematic differences between the sampler and the mean.

Results for the 18 samplers evaluated for the half-day sampling periods are presented in Fig. 5. Because of the logarithmic transformation of the data, the mean squared residual does not give error bounds in terms of neq m^{-3} nitric acid, nor does it correspond to a coefficient of variation. However, the relative com-

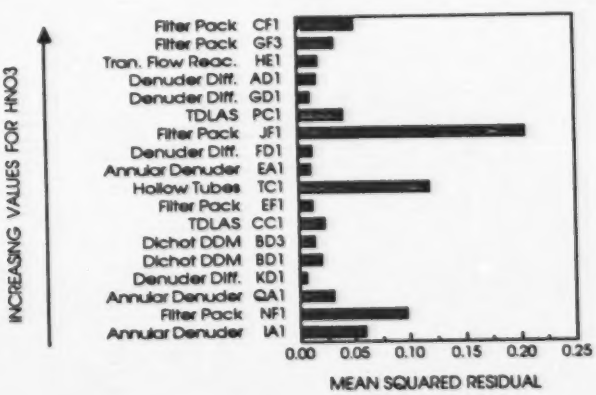

Fig. 5. The measurement precision, as given by the mean squared residual, Equation (1), is shown for eighteen of the samplers. Samplers are listed according to average rank, with those giving the highest nitric acid levels at the top, lowest at the bottom.

parison between samplers is meaningful. We expect the samplers whose nitric acid concentrations are systematically high or systematically low (at the extreme ends of the ordinate in Fig. 5) to have somewhat higher residuals than those samplers in the middle because of the greater systematic difference from the mean.

Two of the samplers, the filter pack no. JF1 and the TAT sampler no. TC1, have very large mean squared residuals. When the daytime and night-time data are examined separately, we find that the nitric acid concentrations reported by the TAT sampler no. TC1 are consistently high at night and low during the day. The opposite is true for the filter pack no. JF1. The diurnal trends in the data from these two samplers can also be seen by close inspection of the time series plots of Figs 2 and 3.

Finally, we wish to quantify the differences among those samplers with relatively small values for the mean squared residual. One possible parameter is the ratio in nitric acid concentrations between samplers. We first examine whether the ratios are a reasonable characterization of the differences between samplers. As an example, in Fig. 6 the ratios for samplers no. BD1 and no. QA1 to the sampler no. HE1 are plotted as a function of the geometric mean nitric acid concentration for each period. The ratios are plotted on a logarithmic scale so that reciprocal ratios (e.g. 2 and 1/2) are equally spaced around the value 1. We find these ratios to be randomly distributed with respect to the nitric acid concentrations, indicating that the ratios are a consistent way to represent the difference between samplers. Although not shown, the ratios between other samplers also appear to be random with respect to nitric acid levels.

As an unbiased estimator of the average ratio between samplers, we have calculated the ratio of mean values, or simply the ratio of the sum of nitric acid concentrations for all the periods considered. These data are given in Table 3. The samplers included in this analysis are the transition flow reactor no. HE1, and the denuded and undenuded dichotomous samplers no. BD1 and no. BD3, all of which operated on the 10- and 12-h sampling schedule. Samplers no. EF1 and no. EA1 collected three samples during the daytime hours, but only one sample at night, and thus can be compared only on the half-day sampling schedule. The other two annular denuders are included for comparison with the annular denuder no. EA1. To provide a comparison with the samplers operating on the 4- and 6-h schedule (Table 4), we have also included the ratios of means of the individual samplers to the mean from the four denuder difference method samplers (DDM). As discussed below, these values parallel the overall sampler mean and the FTIR data.

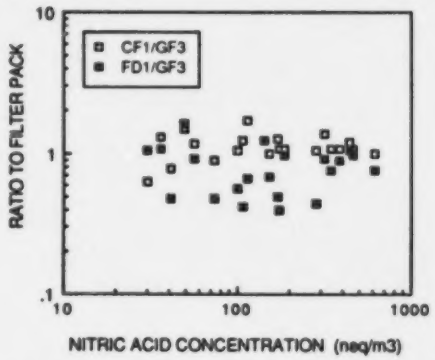

Fig. 6. Concentration ratios between the dichotomous denuder difference sampler no. BD1 and the transition flow reactor no. HE1, and between the annular denuder no. QA1 and the transition flow reactor no. HE1, are plotted against nitric acid concentration. All data are for 10- and 12-h sampling periods.

The sampler pairs marked by asterisks give significantly different results, based on Wilcoxon signed rank tests. This is a non-parametric test used for paired data (Hollander and Wolfe, 1973). It is used to indicate systematic differences between methods. By this test, only the annular denuder no. IA1 and the transition flow reactor no. HE1 were found to differ significantly. Both the denuded and undenuded dichotomous sam-

Table 3. Ratio of means between samplers for nitric acid for 10- and 12-h sampling periods

		$\Sigma y/\Sigma x$							
	x:	HE1	BD1	BD3	EF1	EA1	QA1	IA1	DDM†
y:	HE1	1.00	1.10	1.13	1.24	1.01	1.31	1.74*	1.04
	BD1	0.91	1.00	1.03	1.13	0.92	1.19	1.58	0.94
	BD3	0.88	0.97	1.00	1.10	0.89	1.15	1.53	0.92
	EF1	0.81	0.89	0.91	1.00	0.82	1.05	1.40	0.84
	EA1	0.99	1.09	1.12	1.22	1.00	1.29	1.71	1.02
	QA1	0.76	0.84	0.87	0.95	0.78	1.00	1.33	0.80
	IA1	0.57*	0.63	0.65	0.71	0.58	0.75	1.00	0.60
	DDM†	0.96	1.06	1.09	1.20	0.98	1.26	1.67	1.00

* Samplers differ at > 95% confidence level by Wilcoxon signed ranks (see text).
† Average of denuder difference method samplers no. AD1, no. FD1, no. GD1 and no. KD1.

Table 4. Ratio of means between samplers for nitric acid for 4- and 6-h sampling periods

		Σy/Σx									
	x:	CF1	GF3	AD1	FD1	GD1	KD1	QA1	CC1	PC1	DDM†
y:	CF1	1.00	1.13*	1.31*	1.45*	1.33*	1.60*	1.79*	1.82*	1.78	1.41
	GF3	0.88*	1.00	1.16*	1.28*	1.18	1.41*	1.59	1.60	1.57	1.25
	AD1	0.76*	0.86*	1.00	1.11	1.02	1.22	1.37*	1.38	1.36	1.08
	FD1	0.69*	0.78*	0.90	1.00	0.92	1.10	1.24	1.25	1.22	0.97
	GD1	0.75*	0.85	0.98	1.09	1.00	1.20*	1.34*	1.36	1.33	1.06
	KD1	0.63*	0.71*	0.82	0.91	0.83*	1.00	1.12	1.14	1.11	0.89
	QA1	0.56*	0.63*	0.73*	0.81	0.74*	0.89	1.00	1.01	0.99	0.79
	CC1	0.55*	0.62	0.72	0.80	0.73	0.88	0.99	1.00	0.98	0.78
	PC1	0.56	0.64	0.74	0.82	0.75	0.90	1.01	1.02	1.00	0.80
	DDM†	0.71	0.80	0.93	1.03	0.94	1.13	1.27	1.28	1.26	1.00

* Samplers differ at > 95% confidence level by Wilcoxon signed ranks (see text).
† Average of denuder difference method samplers no. AD1, no. FD1, no. GD1 and no. KD1.

plers, no. BD3 and no. BD1, give statistically equal results. The nitric acid values reported by the transition flow reactor are higher than those from the denuder difference samplers and annular denuders, but are somewhat lower than the no. GF3 filter pack.

COMPARISONS AMONG INDIVIDUAL SAMPLERS: 4- AND 6-h DATA

We compare here nine samplers which collected four 4-h samples and one 6-h sample per day. The set of samplers includes two filter packs, no. CF1 and no. GF3, four denuder difference methods, no. AD1, no. FD1, no. GD1 and no. KD1, one annular denuder no. QA1, and the two diode laser spectrometers, no. CC1 and no. PC1. The TAT system no. TC1 and the annular denuder no. IA1 are not included. The samplers are compared over 15 daytime and six night-time sampling periods (nos 14, 22–24, 31, 33–35, 42–45, 51–55, 61, 63, 73 and 74, as listed in Table A1). For these periods geometric mean nitric acid concentrations ranged from 30 to 616 neq m^{-3}. Periods with geometric mean concentrations below 25 neq m^{-3} (0.6 ppb) are not included in the analysis.

The mean squared residuals for the individual samplers, calculated from Equation (1), are all below 0.05, and are in approximate agreement with the values given in Fig. 5. As with the 10- and 12-h data, the ratios of the nitric acid concentrations reported by different samplers are not dependent upon the nitric acid concentrations, as shown for samplers no. CF1, no. FD1 and no. GF3 in Fig. 7. The characteristic ratio between sampler pairs is estimated by the ratio of means, as given in Table 4. The comparison with the average of the denuder difference method samplers (DDM) is also shown, and provides a basis for comparison with the data of Table 3.

In Table 4 we have also indicated which sampler pairs differ significantly at the 95% confidence level, using the Wilcoxon signed rank test. Significant differences are reported when individual Wilcoxon tests

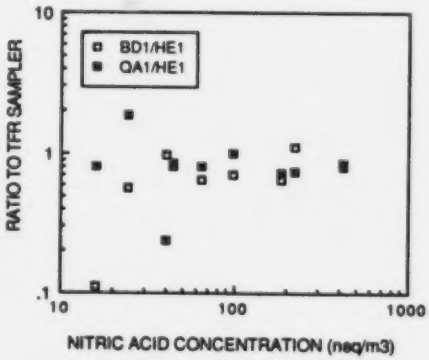

Fig. 7. Concentration ratios between the Canadian filter pack no. CF1 and the Caltech filter pack no. GF3, and between the denuder difference sampler no. FD1 and the filter pack no. GF3 are plotted against nitric acid concentration. All data are for 4- and 6-h sampling periods.

indicate a difference at the > 99.86% confidence level, which for the 36 tests run here corresponds to an overall confidence level of 95%. This test is used to indicate whether one sampler consistently gives higher (or lower) results than the other. Whether or not two samplers prove different depends on the scatter in the data, as well as the magnitude of the difference.

On the average, the highest nitric acid concentrations are reported by the filter pack no. CF1. Its values are significantly higher than those from the other filter pack no. GF3. Both filter packs (no. GF3 and no. CF1) give significantly higher nitric acid levels than the denuder difference and annular denuder samplers. Among the denuder difference samplers, the ratios of means are between 0.8 and 1.2, but only for one pair, no. GD1 and no. KD1, did the difference prove to be statistically significant. The tunable diode laser absorption spectrometers reported lower values, on the average, than the denuder difference samplers and filter packs. The corresponding ratios of means to

the TDLAS are between 1.1. and 1.8. However, the scatter of the data in the comparison of other samplers is such that only the differences in sampler pair no. CF1 and no. CC1 were found to be statistically significant. The annular denuder no. QA1 also gave lower results than the filter packs and denuder difference samplers, and gave the same average value as the tunable diode laser absorption spectrometers.

COMPARISONS WITHIN TYPES OF MEASUREMENTS

The analysis of individual samplers shows that there can be differences among samplers using the same method, as well as among methods. For the filter packs no. CF1, no. GF3, no. JF1, no. EF1 and no. NF1, the Friedman analysis of variance shows differences at the > 99% confidence level. When comparing daytime and night-time sampling periods, sampler no. JF1 is high during the day and low at night. The Friedman analysis of variance shows no significant differences among the six denuder difference samplers, no. AD1, no. BD1, no. BD3, no. FD1, no. GD1 and no. KD1, compared over the 10- and 12-h sampling periods.

Using the Friedman analysis of variance, the nitric acid concentrations measured by the three annular denuders, no. EA1, no. IA1 and no. QA1, differ at > 99% confidence level. Pairwise comparisons using Friedman rank sums show (at the 95% confidence level) that no. IA1 < no. QA1 < no. EA1. The differences are observed for both daytime and night-time sampling.

Figure 3 shows that the two tunable diode laser absorption spectrometers and the two transition flow reactors agree fairly well within methods, while the two TAT systems give quite different results. Each pair of samplers is compared using the Wilcoxon signed rank test. We find no significant differences at the 95% confidence level between the two transition flow reactors and no significant differences between the two TDLAS systems. The two TAT systems differ at the 95% confidence level.

Comparison of 22-h samples with the concurrent sum of 5-per-day samples reveals a potential limitation of the denuder difference method, namely, that the nylon filters become saturated at HNO_3 doses beyond approximately 30 $\mu g\,cm^{-2}$ of filter area. This saturation effect was first reported by Anlauf *et al.* (1986) in another setting. In the present instance, four denuder difference systems were compared, all employing 47 mm dia. nylon filters: (1) no. KD1, collecting 5-per-day samples at flows of 10 and 18 $\ell\,min^{-1}$ through denuded and undenuded branches; (2) no. GD1 and no. GD3, 5-per-day samples but with flows five times less; (3) no. KD2, 22-h samples with flows of 10 and 18 $\ell\,min^{-1}$ and (4) no. GD2, 22-h samples with flows five times less. Good agreement was consistently obtained between (1), (2) and (4). At low HNO_3 concentrations, agreement with (3) was good also. However, on days 3 and 4, when total HNO_3 exposures of the filter on the undenuded side of (3) approached or exceeded 30 $\mu g\,cm^{-2}$, the results from (3) were low, reaching a 37% deficit at an exposure of approximately 35 $\mu g\,cm^{-2}$. These results indicate that HNO_3 exposures of greater than 30 $\mu g\,cm^{-2}$ must be avoided for proper use of the denuder difference method.

Comparisons by Method with the FTIR

In the preceeding sections no comparison was made with the FTIR data because complete data were obtained for only one of the 4-h sampling periods. During other periods either the nitric acid levels were below detection limit, or the FTIR spectrometer was subject to noise interferences. Nevertheless, the FTIR data are of interest because it was the only instrument which did not use sampling lines or filters. Unlike the situation in the 1979 comparison study (Spicer *et al.*, 1982), the optical path for the FTIR in this study was not enclosed within any cell walls. Accordingly, we assume that the FTIR measurements should be less subject to sampling artifacts, and thus comparisons with the other methods are of definite interest.

Rather than comparing individual samplers with the FTIR, we compare the averages of representative samplers for each of the measurement techniques. Values for filter packs (FP), denuder difference methods (DDM), annular denuders (ADM), transition flow reactors (TFR), tunable diode laser absorption spectrometers (TDLAS), and the dichotomous sampler denuder difference method (Dichot) are calculated as follows:

$$\begin{aligned}
FP &= 1/2\{\text{no. CF1} + 1/2\,(\text{no. GF1} + \text{no. GF3})\}\\
DDM &= 1/4\{\text{no. AD1} + \text{no. FD1} + 1/2\,(\text{no. GD1} + \text{no. GD3}) + \text{no. KD1}\}\\
ADM &= 1/3\{\text{no. EA1} + \text{no. QA1} + \text{no. IA1}\}\\
TFR &= 1/2\{\text{no. HE1} + \text{no. DE1}\}\\
TDLAS &= 1/2\{\text{no. PC1} + \text{no. CC1}\}\\
Dichot &= 1/2\{\text{no. BD1} + \text{no. BD3}\}.
\end{aligned}$$

The filter packs are represented by samplers no. CF1, no. GF1 and no. GF3 because each of these samplers used an open face Teflon® filter followed by a nylon filter. Filter pack no. EF1 is not included in the average because it employed a quartz fiber prefilter and thus is not of the same configuration. The other filter packs, no. JF1 and no. NF1, were excluded because of systematic differences between daytime and night-time sampling (no. JF1), errors in chemical analysis (group N), and the large mean squared residual shown in Fig. 5.

The denuder difference method is represented by those samplers using MgO coated denuders. Each of these samplers is preceded by a Teflon® cyclone or a Teflon®-coated cyclone to give a fine particle precut. Some of the DDM samplers use nylon filters; others use Teflon® and nylon filters in series. In all cases nitric acid is given by the difference between the denuded and undenuded sides of the sampler. The dichotomous samplers, which used nylon filters, and operated in

parallel with a nylon filter behind a Teflon®-coated cyclone, also give nitric acid by the difference between denuded and undenuded sample streams. They are listed separately (Dichot) because the principal denuding action is from the aluminum oxide surfaces in the sampler inlet.

The annular denuder method average (ADM) is calculated from all three annular denuders, even though there are statistically significant differences among these samplers. The TFR and TDLAS averages are from duplicate instruments, which, as has been noted, show no significant differences. The FTIR data are represented by one instrument. The tungstic acid technique (TAT) is not included because of the large systematic differences between the two instruments.

Instantaneous data

Instantaneous nitric acid values were reported by the two spectroscopic methods, the FTIR and TDLAS. These data, shown in Fig. 8, represent 5-minute averages from the two TDLAS instruments and are coincident with the most reliable FTIR data during the study period. Fifty-two data points from 14 September ($n = 34$) and 17 September ($n = 18$) are shown in the scatterplot, with the ratio of means TDLAS/FTIR equal to 0.84. At high nitric acid concentrations, the TDLAS data are even lower with respect to the FTIR.

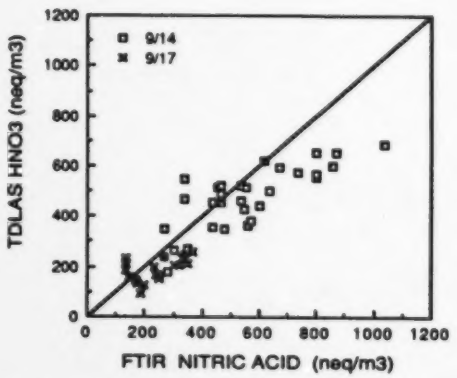

Fig. 8. Comparison of 5-min averages from the two tunable diode laser absorption spectrometers and the FTIR. The line of 1:1 correspondence is shown.

Direct period comparison

Data from one sampling period (1200–1600 PDT on 14 September) permit direct comparison between the FTIR and the non-continuous sampling methods. The corresponding ratios to the reported FTIR period average of 605 neq m^{-3} are 1.32, 1.03, 0.95 and 0.84 for the FP, DDM, ADM and TDLAS, respectively. The closest agreement for this period is the DDM value of 626 neq m^{-3}, which is within 3% of the FTIR value. The FP are higher than the FTIR while the TDLAS is lower. The mean of the FP, DDM, ADM and TDLAS methods is also 626 neq m^{-3}.

Sufficient data were obtained from the FTIR to give hourly average values for two or three of the four hours in sampling intervals 0800–1200 and 1600–2000 PDT on 14 September and for 1200–1600 PDT on 17 September 1986. To obtain a 4-hour average for the FTIR during these periods, the missing FTIR hourly data are estimated by dividing the corresponding TDLAS data by the previously calculated correction factor of 0.84. These values are within the lower and upper bounds for the average concentration calculated by respectively assigning zero and the FTIR detection limit of 160 neq m^{-3} to the missing hourly averages. The upper limit average is expected to be closer to the true period average, especially for the two periods on 14 September when the general level of pollution was high. The averages calculated by scaling to the TDLAS data are close to the upper bound calculation of the average concentrations. Data from the FTIR, TDLAS, FP, DDM and ADM are compared for each of these 4-hour sampling periods in Fig. 9. Error bars show the $\pm$ 160 neq m^{-3} measurement error for the FTIR, as

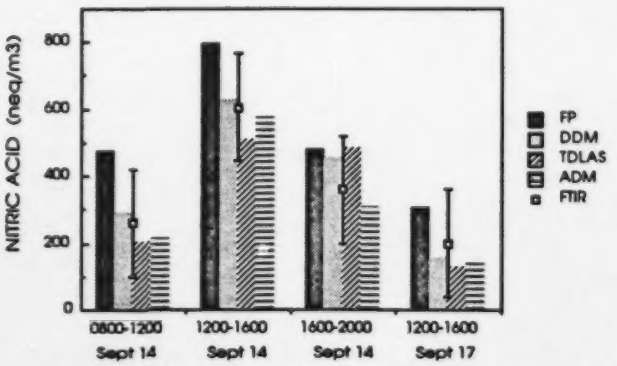

Fig. 9. Methods comparison of nitric acid measurements for the high nitric acid periods of 14 September, and the afternoon period of 17 September. Error bars for the FTIR data correspond to $\pm$ 160 neq m^{-3} ($\pm$ 4 ppb).

reported by Winer *et al.* (1986). For periods with missing data, the additional error is as much as ± 40 neq m^{-3}. While the FTIR data averaged over the four periods are closest to the DDM method mean, all methods agree within their reported range of uncertainty.

Comparisons with the mean of methods

In order to compare reported nitric acid values by method throughout the study we calculated the mean of the methods, weighing the TDLAS, FP, ADM and DDM values equally. Parameters from linear regression of each method against the mean of methods are reported in Table 5. Data for the FP, TDLAS and DDM include 39 of the study periods, whereas the ADM data are for the 23 daytime periods when all three annular denuders were on the same schedule. Also shown is the ratio of each method to the mean of methods. This calculation shows FP values are 36% higher than the mean of the four methods, and that the TDLAS and ADM values are 13 and 21% less than the mean of methods. The ratio of the DDM to the mean of methods is 0.99. In the absence of a reference method for the entire study period, the DDM is chosen as an appropriate basis of comparison, based on this and the previous period comparison with the FTIR.

Day–night comparison by method

Since the DDM value agrees most closely with the mean of the methods and with the FTIR, we have plotted the ratio between each of the methods and the DDM (Fig. 10). The data are shown for the daytime and night-time periods of the study. Some of the data points represent composites of shorter sampling periods while others are from 10- and 12-h samples. For easy comparison, the daytime data are given by open symbols, the night-time data by solid symbols.

On the evening of 16–17 September, the DDM mean appears to be low, as does the Dichot mean. During this period nitric acid concentration was low (DDM mean = 12 neq m^{-3}), and the particle nitrate/HNO_3 ratio was high, which gives a large error in the denuder difference measurements.

Differences occur in the reported nitric acid levels between the TDLAS and other methods during the latter part of the study. On 18 September, a period of intermittent drizzle, the TDLAS data are higher than values from the other methods. The TDLAS data do not exhibit as much diurnal variation as the other methods, and thus with respect to the DDM reported concentrations are higher at night and lower during the day. On 16 September, the TDLAS did not observe the afternoon nitric acid peak measured by other methods. Also, the TDLAS tended to be lower than the DDM at the beginning of the study period, and higher at the end.

Table 6 reports linear regression parameters for the TDLAS, FP, and ADM vs the DDM for the thirty nine 4- and 6-h sampling periods (excluding period no. 64), and for the TFR and Dichot vs the DDM for the 10- and 12-h sampling periods. Noteworthy are the day/night comparisons vs the DDM. The FP, TFR and ADM exhibit no diurnal variation relative to the DDM, while the TDLAS reports markedly higher values at night, averaging 65% higher than the DDM. The FP data are higher than the DDM for night-time as well as daytime sampling. The work of Ellestad *et al.* (1988) and John *et al.* (1988) shows that ammonium nitrate can be lost from Teflon® filters during night-time as well as daytime sampling.

CONCLUSIONS

There are statistically significant, systematic differences in the nitric acid concentrations obtained by the different measurement techniques and sampler configurations employed in the Nitrogen Species Methods Comparison Study. For each sampling period in the study, reported nitric acid concentrations vary among samplers by more than a factor of two, and by as much as a factor of four. For the period with the highest nitric acid levels reported concentrations range from 191 to 800 neq m^{-3}. The standard deviation among all reported values for nitric acid increases linearly with the nitric acid loadings, corresponding to a consistent coefficient of variation of 40%. This variation is much larger than for analysis of the filters upon which known amounts of nitrate had been deposited (better than 11% accuracy for most groups), or for replicate samplers operated by the same group (12 to 27% variability).

Overall, the highest concentrations are from the filter packs, lower concentrations are given by the annular denuders and tunable diode laser absorption spectrometers. Values from the denuder difference method and the transition flow reactors are close to the

Table 5. Linear regression parameters for nitric acid from each method vs the mean of methods

x	y	n	Slope	Intercept (neq m^{-3})	r	$\Sigma y/\Sigma x$
Mean	TDLAS	39	0.75 ± 0.09	17 ± 15	0.94	0.87
Mean	FP	39	1.33 ± 0.07	4 ± 14	0.99	1.36
Mean	ADM	23	0.87 ± 0.05	-15 ± 10	0.99	0.79
Mean	DDM	39	1.07 ± 0.04	-10 ± 7	0.99	0.99

n, number of data points; r, correlation coefficient; $\Sigma y/\Sigma x$, ratio of means. Period no. 64 excluded from analysis.

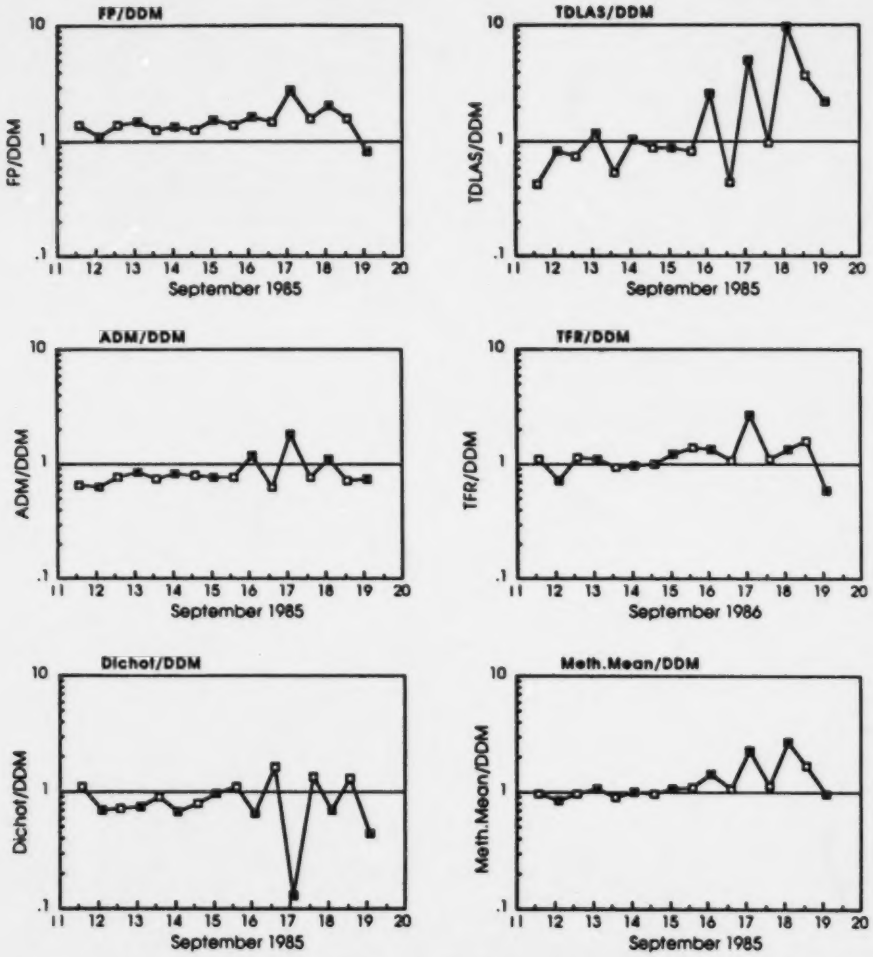

Fig. 10. Ratio of the method means to the MgO denuder difference method mean (DDM) for the day and night-time study periods. Methods shown are filter packs (FP), tunable diode laser absorption spectroscopy (TDLAS), annular denuders (ADM), transition flow reactors (TFR), and the dichotomous sampler denuder difference method (Dichot). Also shown is the mean of the methods with respect to the DDM.

mean of the methods. When the nitric acid concentrations were high enough to be detected by the FTIR, the FTIR values are nearest to those obtained by the denuder difference method; however, values from each method are within the reported uncertainty. The mean FTIR value for the high nitric acid sampling periods is within 3% of the mean of the other methods.

The filter pack method gives higher results for both daytime and night-time sampling. Differences are also seen among the filter packs operated by different groups. Filter pack sampler no. GF3 is higher than the DDM by a factor of 1.25 whereas filter pack no. CF1 is higher by 1.4.

In some cases differences existed in the implementation of the measurement method by different groups, as well as differences between types of measurements. The three annular denuders did not give the same results. Nitric acid concentrations from no. EA1 are greater than from no. QA1, which are greater than from no. IA1 (no. EA1 > no. QA1 > no. IA1). For the two TAT systems, nitric acid concentrations from no. AC1 were greater than from no. TC1. The six denuder difference samplers, including the dichotomous samplers, reported values which were not statistically different from each other. Similarly, values from the two transition flow reactors were not statistically different, nor did the values from the two TDLAS systems differ from one another.

Measurement methods are compared to the average of four denuder difference method samplers. For the annular denuders, the ratio to the DDM value for no. EA1, no. QA1 and no. IA1 are 1.0, 0.8 and 0.6, respectively. For the transition flow reactor the ratio of means to the DDM is 1.09. For the two dichotomous samplers operated as denuder difference samplers, the ratio of means to the DDM is 0.93.

Table 6. Linear regression parameters for nitric acid from each method vs the mean denuder difference measurement

x	y	Period	n	Slope	Intercept (neq m^{-3})	r	Σy/Σx
DDM	TDLAS	All	39	0.68 ± 0.10	26 ± 18	0.92	0.88
		Day	23	0.72 ± 0.14	11 ± 28	0.92	0.77
		Night	16	0.70 ± 0.44	36 ± 25	0.68	1.65
DDM	FP	All	39	1.23 ± 0.08	18 ± 16	0.98	1.37
		Day	23	1.20 ± 0.12	30 ± 29	0.98	1.35
		Night	16	1.35 ± 0.18	5 ± 10	0.98	1.49
DDM	ADM	All	39	0.79 ± 0.05	−1 ± 8	0.99	0.78
		Day	23	0.81 ± 0.07	−7 ± 14	0.98	0.77
		Night*	16	0.73 ± 0.11	5 ± 5	0.97	0.87
DDM	TFR	All	16	1.01 ± 0.10	9 ± 16	0.99	1.09
		Day	8	0.97 ± 0.21	21 ± 40	0.98	1.08
		Night	8	0.95 ± 0.26	7 ± 11	0.97	1.12
DDM	Dichot	All	16	0.86 ± 0.12	8 ± 19	0.97	0.93
		Day	8	0.76 ± 0.22	40 ± 40	0.96	0.97
		Night	8	0.74 ± 0.18	−1 ± 6	0.97	0.71

n, number of data points; *r*, correlation coefficient; Σy/Σx = ratio of means.
Period no. 64 excluded from analysis of 4- and 6-h data.
* For this calculation, the single night-time sample from sampler no. EA1 was split into two samples of equal loadings, so as to match the sample frequency of the other data.

For three of the samplers, there are large differences in the relative performance between daytime and night-time sampling. The TDLAS instruments give low daytime and high night-time readings in comparison to the other measurements. This was most marked on the last three days of the study. Ratios of means to the DDM are 0.77 daytime and 1.65 night-time. The TAT system no. TC1, also is low during the day and high at night. The opposite diurnal response is seen with filter pack no. JF1 which is high during the day and low at night. The FP, ADM, DDM and TFR averages did not exhibit significant diurnal variations with respect to the mean of methods.

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APPENDIX A. DESCRIPTION OF NITRIC ACID MEASUREMENT METHODS

Filter packs (FP). Filter packs were operated by several groups: the Canadian Atmospheric Environment Service (Anlauf and Wiebe, AES, Toronto, Canada), the California Institute of Technology (Cass and Solomon, CIT, Pasadena, CA), Daniel Grosjean and Associates (DGA, Ventura, CA), the Environmental Protection Agency (Martin and Pleasant, EPA, Research Triangle Park, NC) and National Oceanic and Atmospheric Administration (Womack, NOAA, Oak Ridge, TN).

Filter packs use two or more filters in series to remove both particles and gases. Usually a Teflon® filter is used to remove particulate matter, followed by a nylon filter to collect nitric acid. The exact configurations of the filter packs in this study are given in Table 1. The Canadian filter pack contained a citric acid impregnated filter following the nylon filter to collect ammonia. The EPA filter pack has a K_2CO_3 impregnated filter for SO_2 collection. A filter pack operated by Brigham Young University consists of a quartz filter followed by a nylon filter. Most of the filter packs are open faced filters, and thus collected coarse as well as fine particle nitrate. The NOAA filter pack is preceded by a 0.5 m long horizontal elutriator to remove coarse particles.

Denuder difference methods (DDM). Denuder difference method samplers were operated by the Air Resources Board (Horrocks, ARB, El Monte, CA), Brigham Young University (Eatough), California Institute of Technology (CIT, Pasadena, CA, Cass and Solomon), Ford Motor Co. (Pierson and Brachaczek, Dearborn, MI) and two groups (John and Appel) from the Air and Industrial Hygiene Laboratory of the California Department of Health Services (AIHL, Berkeley, CA).

The denuder difference method employs two parallel sampling trains. In one train air is drawn through a diffusion denuder to remove gaseous nitric acid, followed by a nylon filter or a Teflon®-nylon filter pack. The second sampling train is identical to the first except that the denuder is not present. The first sampling train collects particulate nitrate, while the second train collects the sum of nitric acid and particulate nitrate. Nitric acid is obtained by difference. Most of the denuder difference systems used a Teflon® or Teflon®-coated cyclone to give a coarse particle precut, followed by a MgO coated denuder.

Two of the denuder difference samplers (John, AIHL) use a standard Sierra–Andersen dichotomous sampler for the denuded side of the sampling train. The dichotomous sampler filter holders are modified to carry Teflon® and nylon filters mounted in series. In one dichotomous sampler, the aluminum oxide in the inlet of the sampler was tested as a means of removing the nitric acid. A second dichotomous sampler had an annular diffusion denuder of aluminum oxide added to the inlet. Coarse and fine particle nitrate is collected in the dichotomous samplers. A Teflon®-coated cyclone sampler followed by Teflon® and nylon filters in series was used to measure the sum of fine particle nitrate and nitric acid.

Annular denuder method (ADM). Annular denuders were operated by three groups. One system consisting of two annular denuders was operated cooperatively by Research Triangle Institute (RTI, Sickles) and the Italian National Research Council (CNR, Allegrini). Another system of five sequential annular denuders was operated by the University of Calgary (Peake). One annular denuder was operated by Brigham Young University (Eatough).

The annular denuder consists of two concentric glass cylinders coated with a chemical appropriate for the retention of the reactive gaseous species of interest. Air passes through the annular space between the two glass cylinders in a laminar flow where reactive gases are collected by diffusion. This geometry is quite efficient; at equivalent tube lengths and outer tube diameters larger sampling rates can be used than with an open tube denuder. Particles are collected on filters downstream of the denuder.

Upstream of the annular denuders in the RTI/CNR samplers (no. IA1 and no. IA2) a shrouded Teflon® cyclone is used to give a 2.5 μm precut, and a Teflon® manifold is used to split the air flow into each of two identical sampling trains. In each train air passes in series through two 22 cm long Na_2CO_3 coated annular denuders to collect nitric acid, nitrous acid and sulfur dioxide; one 13 cm long citric acid coated annular denuder to collect gaseous ammonia; one Teflon® filter to collect fine particles, one nylon filter to collect volatilized nitrate; and one 13 cm citric acid coated annular denuder to collect volatilized ammonia.

There are two major differences between the annular denuder and the denuder difference method. First, with the annular denuder the gaseous species depositing in the denuder are analyzed directly. Thus nitric acid is obtained directly rather than by the difference of two measurements. The second difference is in the design of the denuder itself.

Transition flow reactor (TFR). This system was operated by two groups, EPA (Ellestad) and Battelle Columbus (Spicer). It is designed for network monitoring of the concentrations of acidic species, which can be used to estimate dry deposition fluxes. Air is drawn through a cyclone which removes particles larger than 2 μm diameter. At the cyclone's outlet, a vortex-removing tee disrupts the spin circulation set up by the cyclone and splits the flow into two 16.1 std ℓ min^{-1} sample streams. Identical sampling trains are used for each of these sample flows. Each 16.1 std ℓ min^{-1} sample enters a tube lined with 3.2 cm long nylon and Nafion strips, which remove 9% of the gaseous nitric acid and 17% of the gaseous ammonia, respectively. Each sample then passes through a Teflon® filter to remove particles, a nylon filter to collect the remaining gaseous nitric acid and any nitric acid gas from the dissociation of ammonium nitrate on the Teflon® filter, and an oxalic acid impregnated filter to collect the remaining ammonia and any ammonia from the dissociation of ammonium nitrate on the Teflon® filter. The flow stream is then split again. The first stream of 1.78 std ℓ min^{-1} flow goes through triethanolamine impregnated glass fiber filters for SO_2 and NO_2 collection and then passes through a flow controller to the pump. The second stream of 14.3 std ℓ min^{-1} passes through another mass flow controller to the same pump. All surfaces in contact with the sample stream are Teflon®.

Tunable diode laser absorption spectrometer (TDLAS). Tunable diode laser absorption spectrometers were operated by the Canadian Atmospheric Environment Service (Anlauf and Wiebe, AES, Toronto, Canada) and by Unisearch Associates (Mackay, Toronto, Canada). The instruments are essentially identical in design, both having been manufactured by Unisearch.

The TDLAS detects species such as nitric acid by infrared absorption in the 2–15 μm region, as described by Hastie *et al.* (1984). Measurements are made utilizing a long-path White cell, operating at approximately 25 torr. The White cell is a Teflon® lined 1 m long, 11.5 cm i.d. pyrex tube. The low pressure is needed to prevent collisional broadening of spectral lines. Ambient air is introduced into the White cell

through a 6 mm o.d., 0.75 mm wall Teflon® tube. Particles are removed by an in-line 0.2 μm pore Teflon® filter located at the entrance of the sampling line. A Teflon® needle valve located downstream of the filter maintains the flow at about 5 ℓ min^{-1}.

Tungstic acid technique (TAT). Two TAT systems were used in the study, one operated by the University of South Florida (Braman), and one operated by the Air and Industrial Hygiene Laboratory (Appel). These are semi-continuous methods which utilize the fact that nitric acid is readily deposited on room temperature tungstic acid-coated surfaces, but at higher temperatures desorbs as an oxide of nitrogen. Air is sampled through a tungstic acid coated preconcentrator tube at 1 ℓ min^{-1} for about 10 min. Then helium carrier gas is introduced while the tube is heated. The deposited nitric acid desorbs as NO or NO_2 and the deposited ammonia desorbs unchanged. Ammonia is then trapped in a WO_x coated transfer tube, while the NO_x passes through to a gold catalyst, where it is converted to NO and detected with a commercial chemiluminescent analyzer. The transfer tube is then heated to desorb the ammonia, which is then oxidized to NO over the gold catalyst and measured by chemiluminescence.

Fourier transform infrared spectroscopy (FTIR). The FTIR was operated by the University of California, Riverside (Winer and Tuazon), to give measurements of ambient nitric acid and ammonia (Tuazon *et al.*, 1981). In this experiment the FTIR used an open multiple reflection optical system with a 25 m basepath, operated at a total pathlength of 1150 m. The entire system was elevated 2.5 m above the ground using large cement headers. Spectra are recorded with a liquid nitrogen cooled HgCdTe detector at 0.13 cm^{-1} spectral resolution using 5-min averaging times. Four to five spectra were obtained per hour. The detection limit for nitric acid in this study was 4 ppb (160 neq m^{-3}).

Luminol HNO_3. This is a semi-continuous method operated by the University of Denver (Stedman, Denver, CO). The total ambient NO_x and nitric acid is measured by passing air through a bed of hot glass beads to a luminol NO_2 detector. The hot beads convert NO and HNO_3 to NO_2. The inlet airstream is alternately chopped with a Teflon® filter and a Teflon®–nylon filter pack. Nitric acid is obtained by the difference between the two signals.

Data listing

The nitric acid concentrations measured by each of the samplers for 4- and 6-h sampling, and for 10- and 12-h sampling, are given in Tables A1 and A2. Samplers are listed by ID nos, as given in Table 1.

Table A1. Nitric acid concentrations reported by each sampler: 4- and 6-h samples

Prd. No.	Sampling time (PDT)		Sampler ID										
			AC1	AD1	CC1	CF1	CF2	EA1	ED1	EF1	FD1	GD1	GD3
12	11 Sept.	0800–1200		16	7	31	34	35	24	19	15	26	20
13	11 Sept.	1200–1600		86	35	150	144	114	32	44	87	85	86
14	11 Sept.	1600–2000		55	31	97	100	92	31	18	75	79	63
15	11 Sept.	2000–0000		19	3	17	20				13	22	10
21	12 Sept.	0000–0600		16	4	12	13				10		
22	12 Sept.	0800–1200		113	85	204	203	75	213	220	69	132	113
23	12 Sept.	1200–1600		139	119	239	261	103	129	198	242	156	134
24	12 Sept.	1600–2000		364	350	474	487	471	185	315	341	306	441
25	12 Sept.	2000–0000		132	110	151	153				20	142	84
31	13 Sept.	0000–0600		55	55	70	63				76	52	35
32	13 Sept.	0800–1200			72	264	215A	202	206	182	134	199	132
33	13 Sept.	1200–1600		439	266	549	466A	299	358	406	446	442	435
34	13 Sept.	1600–2000		497	274	643		506	460	516	566	668	425
35	13 Sept.	2000–0000		165	130	188	166A				128	156	149
41	14 Sept.	0000–0600		113	85	97	93A				78	87	64
42	14 Sept.	0800–1200		408	180	473		231	129	288	198	367	331
43	14 Sept.	1200–1600	429	765	503	795	729A	684	488	670	613	578	
44	14 Sept.	1600–2000	596	503	447	502	448A	423	405	402	431	444	469
45	14 Sept.	2000–0000	391	105	59	102	71A				55	74	73
51	15 Sept.	0000–0600	280	48	16	59	40A				36	52	47
52	15 Sept.	0800–1200	286	260	138	304	240A	203	430	231	113	187	185
53	15 Sept.	1200–1600	362	295	247	503	367A	298	240	410	332	327	465
54	15 Sept.	1600–2000	261	155	154	221	208A	181	147	121	197	206	218
55	15 Sept.	2000–0000	123	11	55	52	50A				43	16	34
61	16 Sept.	0000–0600	93	16	55	24	24A				40	25	15
62	16 Sept.	0800–1200	47	95	26	47	60A	21	287	315	33	110	
63	16 Sept.	1200–1600	123	147	42	307	234A	149	31	167	120	175	
64	16 Sept.	1600–2000	103	89		87	85A	71		39	112	83	
65	16 Sept.	2000–0000	52	26	30	22	25A				2	10	
71	17 Sept.	0000–0600		31	89	47	43A				7	2	
72	17 Sept.	0800–1200	61	98	30	48	50A	15	58	26	0	0	
73	17 Sept.	1200–1600	121	163	140	344	274A	184	110	250	134	159	
74	17 Sept.	1600–2000		89	119	137	144A	86		78	73	111	
75	17 Sept.	2000–0000	103	13	65	27	30A				10	2	
81	18 Sept.	0000–0600		10	81	18	18A				8	10	
82	18 Sept.	0800–1200	96	11	55	25	22A	8	33	11	7	0	
83	18 Sept.	1200–1600	119	31	119	55	43A		26	22	26		
84	18 Sept.	1600–2000	161	19	82	23	19A	28	20	10	30	5	
85	18 Sept.	2000–0000	166	5	43	12	8A				0	16	
91	19 Sept.	0000–0600	166	5	4		6A				6	32	

Table A1. (*Contd.*)

Prd No.	Sampling time (PDT)		Sampler ID										
			GF1	GF3	IA1	IA2	KD1	MF1	PC1	QA1	RC1	SC1	TC1
12	11 Sept.	0800–1200	15	26	4	3	15			3			12
13	11 Sept.	1200–1600	83	104	14	16	89	139		7		113	10
14	11 Sept.	1600–2000	71	82	29	16	62	108	32	37		82	33
15	11 Sept.	2000–0000	23	12	14	10	18	18	28	8		111	38
21	12 Sept.	0000–0600			3	3	5		9			92	21
22	12 Sept.	0800–1200	134	165	37	38	88	79	57	130		155	59
23	12 Sept.	1200–1600		194	69	44	107		76	92		129	71
24	12 Sept.	1600–2000	468	441	177	168	348	482	239	290		283	153
25	12 Sept.	2000–0000	147	122	68	40	65	129		108		249	120
31	13 Sept.	0000–0600	71	46	21	24	32	66	59	25		70	80
32	13 Sept.	0800–1200	179	196	53	51	111		50	132			96
33	13 Sept.	1200–1600	485	500	268	191	367		228	330			186
34	13 Sept.	1600–2000	606	586	321		466		262	371			208
35	13 Sept.	2000–0000	180	187	74		122		178	127			168
41	14 Sept.	0000–0600	115	113	42		49			77			127
42	14 Sept.	0800–1200	492	452	182		218		227	226	260		139
43	14 Sept.	1200–1600	788	800	511		547		514	524	605	305	191
44	14 Sept.	1600–2000	498	412	168		423		518	325	360	243	188
45	14 Sept.	2000–0000	104	114	58		57		53	72			145
51	15 Sept.	0000–0600	74	75	31		19		63	40			93
52	15 Sept.	0800–1200	302	283	88		139		132	129		203	
53	15 Sept.	1200–1600	406	358	204		327		255	255		149	75
54	15 Sept.	1600–2000	224	203	120		183		214	154		98	52
55	15 Sept.	2000–0000	59	39	18		29		82	49			64
61	16 Sept.	0000–0600	42	38	12		12		55	40			59
62	16 Sept.	0800–1200	67	55	22		−12		50	27		203	77
63	16 Sept.	1200–1600	270	178	79		120		39	109		80	75
64	16 Sept.	1600–2000	116	100		9	72			60		45	57
65	16 Sept.	2000–0000	21	20			10			19		90	39
71	17 Sept.	0000–0600	42	35			7		99	19		33	36
72	17 Sept.	0800–1200	62	15		12	−3		60	23		51	51
73	17 Sept.	1200–1600	273	272		115	178		117	120	200	50	71
74	17 Sept.	1600–2000	105	129		102	88		134	59		23	60
75	17 Sept.	2000–0000	6	7		8	13		107	15		15	22
81	18 Sept.	0000–0600	24	18		3	6		94	8		19	23
82	18 Sept.	0800–1200	28	25	4	5	5	26	39	11		39	26
83	18 Sept.	1200–1600	52	7	10	11	24		77	29		39	20
84	18 Sept.	1600–2000	13	8	9	7	13	29	36	18		38	19
85	18 Sept.	2000–0000	9	7	5	6	3	60		6		22	13
91	19 Sept.	0000–0600	12	10	4	3	5	8	18	7		11	8

*Sampler ID nos are given in Table 1.
'A' indicates an average of several samples of shorter duration.

Table A2. Nitric acid concentrations reported by each sampler: 10- and 22-h sampling periods

Table A2. Nitric acid concentrations reported by each sampler: 10- and 22-h sampling periods

Prd No.	Starting date	Sampling time (PDT)	Sampler ID												
			AC1	AD1	BD1	BD3	CC1	CF1	DE1	EA1	ED1	EF1	FD1	GD1	GD3
16	11 Sept.	0800–2000		52A	64	64	24A	93A	61	53	29A	27A	59A	63A	56A
17	11 Sept.	2000–0800		17A	8	12	3A	14A	8	10		8	11A		
26	12 Sept.	0800–2000		205A	150	150	185A	306A		211	176A	244A	217A	198A	229A
27	12 Sept.	2000–0800		86A	47	51	77A	102A		75	158	55	54A	88A	55A
36	13 Sept.	0800–2000			330	328	204A	485A		415	341A	368A	382A	436A	330A
37	13 Sept.	2000–0800		134A	68	73	103A	133A	101	100	64	75	98A	114A	98A
46	14 Sept.	0800–2000		559A	382	355	377A	590A	463	550	377	433	414A	463A	
47	14 Sept.	2000–0800	325A	71A	49	51	33A	76A	67	25	41	32	44A	61A	58A
56	15 Sept.	0800–2000	303A	237A	267	244	180A	343A	399	191	272A	254A	214A	240A	289A
57	15 Sept.	2000–0800	105A	14A	13	17	55A	35A	42	24	16	15	41A	22A	23A
66	16 Sept.	0800–2000	91A	110A	161	151	36A	147A	101	70		173A	88A	123A	
67	16 Sept.	2000–0800		29A	0	5	65A	37A	41	25		19	5A	6A	
76	17 Sept.	0800–2000		117A	136	138	96A	176A	101	95		118A	69A	90A	
77	17 Sept.	2000–0800		11A	4	10	75A	22A	11	13		7	9A	7A	
86	18 Sept.	0800–2000	126A	20A	23	24	85A	34A	36	22	27A	14A	21A		
87	18 Sept.	2000–0800	166A	5A	4	4	19A		13	13	7	7	4A	25A	

Prd No.	Starting date	Sampling time (PDT)	Sampler ID											
			GF1	GF3	HE1	IA1	IA2	JF1	JF2	KD1	NF1	PC1	QA1	SC1	TC1
16	11 Sept.	0800–2000	56A	71A	65	16A	12A	31	0	56A	24	32A	16A		21A
17	11 Sept.	2000–0800			12	8A	6A	0	0	10A	9	17A		100A	27A
26	12 Sept.	0800–2000		266A	234	94A	83A	317	305	181A	238	101A	171A	189A	91A
27	12 Sept.	2000–0801	101A	77A	73	40A	30A	44	51	45A	67	59A	58A	142A	89A
36	13 Sept.	0800–2000	424A	427A	341	214A		523	501	315A	318	180A	278A		162A
37	13 Sept.	2000–0800	141A	142A	96	55A	50	86	84	78A	56	178A	97A		142A
46	14 Sept.	0800–2000	593A	555A	446	287A	10	781	762	396A	333	420A	358A		169A
47	14 Sept.	2000–0800	86A	91A	62	42A	27	11	28	34A	9	59A	53A		117A
56	15 Sept.	0800–2000	311A	282A	239	137A	165	499	479	216A	238	200A	179A	150A	64A
57	15 Sept.	2000–0800	49A	38A	23	14A	11	0	0	19A	29	66A	44A		61A
66	16 Sept.	0800–2000	151A	111A	104			149	201	60A	149	48A	65A	110A	70A
67	16 Sept.	2000–0800	34A	29A	23		7	0	0	8A	57	99A	19A	56A	38A
76	17 Sept.	0800–2000	147A	139A	121	56	76A	151	175	88A	29	104A	67A	42A	61A
77	17 Sept.	2000–0800	17A	14A	14	5	5A	0	0	9A	19	99A	11A	17A	23A
86	18 Sept.	0800–2000	31A	13A	23	8A	7A	0	0	14A	16	51A	19A	39A	21A
87	18 Sept.	2000–0800	11A	9A	0	5A	4A	0	0	4A	5	33A	7A	15A	10A

* Sampler ID nos. are given in Table 1.
'A' indicates an average over several samples of shorter duration.

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